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CHROMIC ACID AS A SOLVENT FOR GOLD

BY

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THESIS

FOR THE

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IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Henry William Hachmeister,

ENTITLED Chromic Acid As A Solvent For Gold,

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor Of Science.

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HEAD OF DEPARTMENT OF Chemistry.

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CHROMIC ACID AS A SOLVENT FOR GOLD.

The use of a chromic acid solution as a solvent for gold seems to have received but little consideration, for apparently there seems to be but one mention of it in the literature. Classen[10] in his text on Quantitative Chemical Analysis of Electrolysis, states, "According to a private communication of Dupri, of Strasfurt, gold may be readily removed from platinum electrodes by warming with a solution of chromic acid and sodium chloride." Classen recommends this solution for such purpose and states that the platinum is not attackt although the gold is. What this action is due to, or what reaction takes place in the solution of the gold he does not try to explain, nor does he tell how to recover the gold from the solution of chromic acid and salt.

The only work treating to any extent of this solvent action is the thesis of Thomas Bailey,[1.] University of Illinois, 1905, entitled "Solvents for Gold." He followed along the line of work started by Victor Lehner of the University of Wisconsin on the "Action of Oxidizing Agents on Gold."[3] Bailey extended the work to include chromic acid as one of the oxidizing agents. It is probable that extensive work has been done on solvents for gold, but, as little has been published along this line, it seems that the results have been unsatisfactory or have been kept secret for commercial reasons. It is certain that the commercial possibilities for a better method than those now used, would be great,

for it would open a new field, that of recovering the gold in ores of too low grade to be worked by either of the methods now employed.

There are at present only a few methods employed for the recovery of gold in ores by wet processes. The most important of them are, the potassium cyanide[5] method, the chlorination method[4] and the Von Patera[8] or thiosulphate method, the latter being the most important wet process for the treatment of silver ores and is important as it dissolves gold sulphide.

Since the solution of chromic acid and sodium chloride dissolves gold it was thought possible to use it commercially to recover gold from ores of low grade. To be used commercially a wet process requires that the solvent be of low cost, complete as to solvent power, easily handled and washed. It must also be possible to use continuously without deterioration and applicable to ores as they occur or may be brought into condition by cheap and handy methods such as roasting and etc. The methods now employed are of the above nature but have their limitation in that neither the potassium cyanide nor the chlorination methods can be used for ores containing combined gold without being roasted beforehand, neither can the potassium cyanide method which is the only one applicable to low grade ores be used, for ores running lower than two and one half dollar per ton, with profit.[6]

Even if not adapted to commercial purposes it may still be true that a theoretically correct method may serve a good purpose as a laboratory method in the assay of low grade ores where large quantities of materials must be employed to obtain

results of any value. There are only two methods used at present for the wet assay of gold ore. They are the extraction by potassium cyanide and the chlorination method. These methods are not exactly accurate as both dissolve only the free gold and at that generally only about 80 to 90% of the total gold present. They are both used as laboratory tests in connection with the extraction of gold from ores by the cyanide and chlorination processes to determine the percent of extraction on a small scale and to determine the adaptability of an ore to the method and whether or not it can be economically treated. Assay by fire is the method most generally used, being the most accurate and rapid and giving results, except in ores running lower than one tenth of an ounce to the ton, which are correct within three tenths of one percent. Several methods for the wet assay of copper mattes, copper, and gold bullion can be found in the literature but few for the wet assay of gold ore, none of which are recommended for exact assay.

It was therefore considered of importance to find out whether or not this solution could be used for the commercial and laboratory extraction of gold from ores and if so to devise a method by which this could be accomplished with the greatest ease and accuracy. To determine this the following work was done.

TREATMENT OF THE ORES.

The method of proceedure was as follows: The material used was a talcose ore, a hydrated silicate of magnesia, ($3\ Mg\ O$, $4\ Si\ O_2$, H_2O), a fair sample of free milling gold ore. The gold in this ore was in the state of minute particles, some being large

enough to be seen with the naked eye. The ore was pulverized and passed through a hundred mesh sieve before treatment and thoroughly mixed. One assay ton of the ore was taken in all instances and treated with varying amounts of a solution, containing five percent of chromic acid and ten percent of common salt, at various temperatures. The percent of extraction was determined by assaying the tailings or ore after treatment. The following data shows the effect of time, temperature and amount of solution, on the percent of extraction:

Case 1.

To one assay ton of the ore were added 100 c.c. of the solution and the mixture digested on the steam bath for four hours. The solution was then filtered on a Bruckner funnel and washed. The residue was dried and assayed. Two samples were treated in this way and the mean taken, and it was found that .00016 gms. of gold had been extracted and as the sample contained .00244 gms. to begin with the percent of extraction was 6.55

Case 2.

150 c.c. of the solution were added to one assay ton of ore and digested on the steam bath for four hours. The residue showed that .00123 gms. had been extracted or 50.41 percent.

Case 3.

One assay ton was treated with 100 c.c. of the solution for two hours at boiling temperature or 101° C. The gold extracted was found to be .00125 grams or 51.23 percent.

Case 4.

100 c.c. of the solution was added to one assay ton of

ore and digested at 101° for one hour. The residue showed that .00086 gms. had been extracted or 38.88 percent.

Case 5.

The ore was treated with 200 c.c. of the solution and boiled for three hours. The residue showed that .00111 gms. of gold had been extracted or 45.50 percent.

Case 6.

The ore was treated in this case with 100 c.c. of the solution and one c.c. of concentrated sulphuric acid and boiled for two hours. The residue showed an extraction of 81.56 percent or .00198 grams of gold had been dissolved.

Case 7.

The ore was treated with 200 c.c. of the solution and four c.c. of the concentrated sulphuric acid and boiled for two hours. The residue showed that .00216 grams of the gold had been extracted or 88.52 percent.

Case 8.

The ore was treated with 200 c.c. of the solution and four c.c. concentrated sulphuric acid and boiled for three hours. The residue showed no trace of gold so that the percent extraction was 100 percent.

Case 9.

The ore was treated with 250 c.c. of the solution and two c.c. concentrated sulphuric at boiling temperature for two hours. The residue showed that .00234 grams had been extracted or 96.02 percent.

Case 10.

The ore was treated with 250 c.c. of the solution and 4 c.c. concentrated sulphuric acid at boiling temperature for three hours. The residue showed that .00239 grams of gold had been extracted or 98.00 percent.

Case 11.

The ore was treated with 250 c.c. of the solution at boiling temperature for two hours. The residue showed but a small trace of gold too small to be weighed, or in other words a perfect extraction.

All the preceeding results show that the percent of extraction increases with the volume, temperature and time. The best results being obtained when the solution is boiled for this mixture is constantly agitated and the ore is thus continually being brought into contact with the solvent. That a small amount of sulphuric acid greatly adds to the solvent power of the solution is well brought out by the increase shown between cases 5 and 6 where one c.c. of the acid changed the percent of extraction from 45% to 81%. That further increasing the amount of acid changes the solvent power but little more is well brought out by cases 6 and 7. Increase in time is the most important factor in all cases. The percent of deterioration was determined by titrating the solution before and after using with a solution of sodium-thiosulphate, the value of which is known in terms of chromium trioxide. It was that the percent deterioration varied but little, varying from 4 to 12 percent, except in the last case where it ran up to 18.5 percent.

In the above work nothing was said about the amount of silver that was extracted and it may be interesting to note that the extraction increases very much with the time, volume and percent of sulphuric acid present. The extraction varied from 50 to 86 percent.

For the study of the above cases in a more convenient form for comparison the results are tabulated as below.

Table I

Time Hours	Volume of Solution	Temp.	Gold in Sample	Gold Extracted	% ex-tracted	cc H_2SO_4	
4	100	Steam Bath	.00244	.00016	6.55	0	
4	150	"	.00244	.00123	50.41	0	
2	100	101°	.00244	.00125	51.23	0	
1	100	101°	.00244	.00086	38.88	0	
3	200	101°	.00244	.00111	45.50	0	
2	100	101°	.00244	.00198	81.56	1 c.c.	#
2	200	101°	.00244	.00216	88.52	4 c.c.	
3	200	101°	.00244	.00244	100.	4 c.c.	#'
2	250	101°	.00244	.00234	96.02	2 c.c.	
3	250	101°	.00244	.00239	98.00	4 c.c.	+
2	250	101°	.00244	.00242	100.	10 c.c.	

REMARKS.

note effect of acid

#' note effect of time.

+ note small increase caused by excess of acid, time being the most important item.

RECOVERY OF THE GOLD DISSOLVED IN THE CHROMIC ACID SOLUTION

The precipitation or removal of the gold from the solution is a problem which naturally follows the solution of the gold. If the method is to be of any commercial value the removal of the gold must be accomplished without destroying the dissolving power of the solution, and if it is to be used as a laboratory solvent, the removal must be complete. To determine the most effective means for doing so, the following experiments were performed. The solutions used for this work were the filtrates obtained in the extraction of the ore and were of known gold content.

Bailey found that calcium hydroxid throws the gold out of solution as a black amorphous powder and claims that precipitation is almost complete, only a trace of gold being retained by the solution. A number of tests were therefore run to determine the effectiveness of this method and to check Bailey'S results. It was found, however, that in no case was the removal greater than 86 percent, while in some cases it was very low. The removal of the gold depends somewhat on the amount of calcium hydroxid added as does also, the percent deterioration. If enough is added to neutralize the solution, the oxididation power of the same is almost completely destroyed, while the precipitation is the highest. These results do not correspond to Bailey, the reason for which could not be determined.

To see if the other hydroxides of the alkaline earths had the same effect, barcium hydroxide was next tried. The solution contained .00216 grams of gold and Ba (OH)$_2$ was added to

make the solution slightly alkaline. The precipitate was filtered off, dried and assayed. It was found that only a trace of gold came down, while the solution completely lost its oxidizing power. Barium chromate is formed, which being insoluble, forms the greatest part of the precipitate. Barium chloride and sodium carbonate were also tried but in both cases the precipitate was free from gold. This shows that the solution can be destroyed without precipitating the gold.

Hydrogen sulfide in slightly acid solution, removes the gold completely, precipitating it as the insoluble sulfide of gold. The solution must be comparatively dilute, otherwise, sulphur separates out, which is not easy to handle. The following results show the completeness with which hydrogen sulfide removes or precipitates the gold from chromic acid solution.

Solution contained		.00111	grams Au.
Hydrogen sulfide		.00108	" "
"	" pp't removed	98.00 %	"
Solution Contained		.00111	grams Au.
Precipitate "		.00104	" "
"	"	92.50%	"
Solution contained		.00162	grams Au.
Precipitate "		.00160	" "
"	"	99.00%	"
Solution contained		.00162	grams Au.
Precipitate "		.00162	" "
"	"	100%	"

These results are but a few of those collected but they show that hydrogen sulfide removes the gold quantitatively. The solution is however completely reduced which destroys the value of this method for commercial use. The gold in this case is recovered by scorifying.

Hydrogen sulfide in ammoniacal solution, also precipitates the gold. The $Cr_2(O3)_6$ upon the addition of H_2S is changed to $Cr(SO4)_3$, by the reducing power of the hydrogen sulfide and precipitates as $CrOH_3$ with the amorphous gold powder. Sulphur also separates out, due to the decomposition of the H_2S.

Bailey shows that metallic mercury on being shaken with the solution removes the gold which is left behind as a black amorphous powder, when the mercury is dissolved in nitric acid, or distilled off. The mercury has a bad effect upon the solution, the strength of which deteriorates from 8 to 15 percent, depending on the length of time the solution is left in contact with mercury. Copper plates were amalgamated with mercury and suspended in the solution for various lengths of time. It was found that the mercury was oxidized and the gold left in bright spots on the copper plates.

Alcohol and formaldehyde reduce the gold and also the solution. The gold is precipitated as metallic gold, and in some cases a gold mirror is found on the side of the vessel containing the solution.

Oxalic acid and ferrous sulphate do not precipitate the gold as would be expected, but destroy the solution.

The electric current was tried to remove the gold from solution, but was unsuccessful. In some cases a trace of gold

is deposited on the cathode but more it does not deposite. With a revolving cathode and a current of .3 to .5 amperes and 3 to 5 volts, metallic chromium will deposite from the neutral chromic acid solution, but not when any sulphuric acid is present. During electrolysis chlorin gas is given off, which if left there would entirely change the nature of the solvent.

The above facts show that no method was found by which the gold could be removed without destroying the oxidizing power of the solution. Before the solution can be used commercially, such a method must be devised. That this solution might be used to advantage on the acid ores seems possible and would if successful soon replace the cyanide method which is not well suited for ores containing free acid, large amounts of lime being used to maintain the neutrality of the solution. The chromic acid works best in acid solution and would be thus suited to natural conditions. It is certain, however, that before any thought can be given to its commercial application, a good method must first be found to recover the gold without deteriorating the solution, so as to allow continuous use.

This fact, however, does not affect its value as a laboratory solvent and the following method was worked out to use in the wet assay of low grade gold ores. The method is as follows: Weigh out two assay tons of pulverized ore, (60 to 100 mesh fine), in a beaker and add 400 C.c. chromic acid solution, containing five per cent chromic acid and ten per cent salt, and 5 c.c. con. sulphuric acid. Place on a hot plate and boil from three to four hours. Remove and filter hot, through a Bruckner funnel, using suction and wash several times with water. Cool and pass hydrogen sulfide through solution until saturated, and

filter. Dry precipitate and recover gold by scorification and cupellation. It will be found that the above method is accurate and checks with results obtained by five assay. It is however, only accurate for gold as the silver is neither dissolved or precipitated quantitatively.

A further study of the action of the above solvent on platinum was made in order to verify the statement of Classen's that no dissolving of the platinum occurs. This further had the purpose of indirectly indicating the reaction between the solvent and gold. It must be evident that if free chlorin is generated by the mixture of chromic acid and salt and chromic acid, salt and sulphuric acid, that element would account for the solvent action on the gold. Furthermore, if free chlorin be present, that fact would be made evident by the study of its action in absence of gold. The results of this study are shown in the table below.

Platinum — Table II — 200 c.c. (5% CrO_3 (10% NaCl.

Time	c.c. H_2SO_4	Weight Before	Weight After	Grams Dissolved	Temp.	Area of Surface
1 Hours	none	3.3202	same	.0000	101°	
3 "	"	"	"	.0000	"	
5 "	"	"	3.3201	.0001	"	
65 "	"	3.3201	3.3200	.0001	32°	
1 "	4 c.c. Acid	3.3200	same	.0000	101°	
3 "	"	"	"	.0000	101°	
48 "	"	"	"	.0000	30°	
24 "	10 "	"	"	.0000	"	
60 "	10 "	"	"	.0000	"	

Gold — Table III — 100 c.c. (5% CrO_3, 10% NaCl)

Time	c.c. H_2SO_4	Weight Before	Weight After	Grams Dissolved	Temp.	Area of Surface
1 hour	none	.2668	.2540	.0128	101°	
3 "	"	"	.2315	.0353	"	
5 "	"	"	.1981	.0687	"	
65 "	"	.1981	.1716	.0265	32°	
48 "	4 c.c. acid	.1716	.1498	.0218	101°	
3 "	"	"	.1200	.0516	"	
48 "	10 "	.1200	.1006	.0194	30°	

Suggested reactions for the solution of gold by chromic acid solution and reaction in the solution due to the various ingredients.

$$CrO_3 + H_2O = H_2CrO_4$$

$$H_2CrO_4 + NaCl = Na_2CrO_4 + 2HCl.$$

$$2Na_2CrO_4 + 2HCl = 2NaCl + Na_2Cr_2O_7 + H_2O$$

$$Na_2Cr_2O_7 + 8HCl = Cr_2Cl_6 + 2NaCl + 3O + 4H_2O.$$

$$2Au + 3O = Au_2O_3.$$

As there is no better reason for excepting this last equation asthe source of oxygen than the first, hence the reaction is still in doubt.

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